Evaluation a Novel Secondary Disinfectant Formulation that Reduces Disinfection By-products

Project Scope

This research addressed two critical issues associated with the use of a new secondary disinfectant formulation composed of hydrogen peroxide (H_2O_2) and silver ion (Ag^+): (1) the efficacy of long-term residual disinfection, including the control of coliform bacteria, bacterial regrowth, and slime/biofilm control; and (2) the identification and quantification of disinfection by-products (DBPs) that may result from interactions with conventional chlorine- and oxidant-based primary disinfectants. The H_2O_2/Ag^+ disinfectant formulation is commercially available and designed for use after a strong primary disinfectant. It has been approved as a drinking water disinfectant in Switzerland, Germany, and Australia. By combining two or more disinfectants, it may be possible to lower concentrations of each component, reduce exposures, minimize the formation of toxic and undesirable DBPs, and thus minimize health risks associated with disinfection. In addition to reduced DBPs, when compared to chlorine as a secondary disinfectant, the combined H_2O_2/Ag^+ disinfectant provides long-lasting residual disinfection and presents a low health risk.

The goal of this research project was to develop information regarding disinfection efficacy and DBP formation associated with the H_2O_2/Ag^+ and silver disinfectant formulation using a range of source waters under a variety of conditions common in drinking water treatment utilities.

The research consisted of the following sets of experiments:

- A laboratory evaluation of microbial disinfection efficacy by optimizing formation of the secondary disinfectant combination and total doses of primary and secondary disinfectants;

Grant Title and Principal Investigators

Evaluation of the Efficacy of a New Secondary Disinfectant Formulation Using Hydrogen Peroxide and Silver and the Formulation of Disinfection By-products Resulting From Interactions with Conventional Disinfectants (EPA Grant #R825362)

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Key Findings and Implications

Key Findings:

- The bacterial inactivation performance of hydrogen peroxide and silver (H_2O_2/Ag^+) as a disinfectant was as effective as chlorine-based disinfection, but slower.
- Virucidal action of H_2O_2/Ag^+ was observed when used as a disinfectant and biofilm control efficacy over long periods was limited.
- The addition of the H_2O_2/Ag^+ secondary disinfectant following the use of chlorine or ozone as a primary disinfectant resulted in dramatic reductions in disinfection by-products (DBP) formation. Hydrogen peroxide appears to quench formation of the major DBPs by reducing free chlorine concentrations.

Implications of Research:

- The combined disinfectant may be appropriate for use as long-term secondary residual disinfectant for relatively high quality water.
- Results from a series of risk assessments indicated that human health risks resulting from the use of the H_2O_2/Ag^+ as a secondary disinfectant, in even "worst case" exposure scenarios, would be minimal.

Publications include 8 peer reviewed articles and 6 conference/workshop presentations.

Project Period: June 1997 to June 2000

Relevance to ORD's *Drinking Water Research Multi-Year Plan* (2003 Edition)

This project contributes directly to the first of three Long-term Goals for drinking water research: (1) by 2010, develop scientifically sound data and approaches to assess and manage risks to human health posed by exposure to regulated waterborne pathogens and chemicals, including those addressed by the Arsenic, M/DPB, and Six-Year Review Rules.

This research suggests that the combined hydrogen peroxide/silver disinfectant may be appropriate for use as long-term secondary residual disinfectant for relatively high quality water. This research also suggests that a multiple component disinfectant combination applied sequentially might provide effective inactivation and reduced by-product formation. The research results provide information to assess risk management options and to evaluate future policies and decisions regarding disinfection approaches.

- A laboratory evaluation of DBP formation resulting from interactions with various primary disinfectants;
- An evaluation and possible field-scale demonstration of the combined disinfectant; and
- Related studies designed to evaluate potential risks and other aspects associated with the H_2O_2/Ag^+ disinfectant and any formed DBPs.

Investigations measured the inactivation performance of a combined disinfectant comprised of H_2O_2 and silver or copper ions for target indicator microorganisms in both synthetic high quality water and in high-total organic carbon (TOC) water (TOC = 6 mg/L). Die-off kinetics were evaluated upon exposure to H_2O_2, silver or copper ions alone, and in combination. Target or model organisms included bacteria (*Escherichia coli-B* and *Escherichia coli-K12*), bacteriophage (MS2), and a pathogenic virus (Polio 1).

Project Results and Implications

Bacterial Inactivation: The combination of hydrogen peroxide and silver ions, rather than tested separately, was determined to be the most effective in inactivating *E. coli-B* and *E. coli-K12*. Silver ion was more effective than H_2O_2 when used in isolation. In general, the rate of bacterial inactivation of the combined disinfectant was slow compared to chlorine-based disinfectants (e.g., 3-log reductions of *E. coli-B* at the optimized formulation required an exposure of 77 minutes compared to 15 minutes using 1 ppm chlorine). Inactivation of *E. coli-B* in water containing 6 mg/L TOC (high quality water) was 3-fold less than inactivation in synthetic water. Inactivation performance of the combined disinfectant improved at basic pH (e.g., 2-fold log difference inactivation between pH 6 and 9 using the optimized formulation). Inactivation performance also improved with temperature (e.g., 2-fold greater log inactivation of *E. coli* 24 C° compared to 4 C° for a 1-hour exposure to the optimized formulation). Inactivation of *E. coli-B* at pH 7 after 1 hour of exposure at room temperature to 125 ppb copper ions showed less than 1-log reduction. However, 4.3 logs reduction were obtained during the same time interval in combination with 30 ppm H_2O_2. The synergistic interaction of H_2O_2 with copper ion was greater than with silver ions.

Viral Inactivation: The combined disinfectant showed rather slow viral inactivation kinetics. Approximately 6 hours were necessary to achieve 4 logs inactivation of MS2 bacteriophage at 24 C° and pH 7 using a rather high concentration of the combined disinfectant (100 ppm H_2O_2 and 100 ppb silver ion). Inactivation of the MS2 virus was achieved exclusively by the H_2O_2 ingredient; the virus was found to be unaffected or even perhaps even protected by the presence of the silver ions. The inactivation of Polio 1 virus was even slower—0.15 log reduction was obtained by 12 hours exposure to the same combined disinfectant.

Biofilm Control: Biofilm control using approximately 1 ppm of chlorine was shown to be considerably higher than that for the H_2O_2/Ag^+ disinfectant. The bacteria that survived after 48 hours disinfection with

H_2O_2 alone and the H_2O_2/Ag^+ disinfectant showed high catalase activity, suggesting that H_2O_2 and H_2O_2/Ag^+ disinfectant may have a rather limited effectiveness in controlling biofilm growth during continuous operation. Based on these results, the researchers concluded that the full-scale field demonstrations originally envisioned would not be warranted.

Disinfection By-Products: The addition of the secondary disinfectant following the use of chlorine or ozone as a primary disinfectant was shown to produce dramatic reductions in DBP formation. Using chlorine, the H_2O_2/Ag^+ secondary disinfectant diminishes the formation of trihalomethanes (THMs) and haloacetic acids (HAAs)—two groups of DBPs that have been priorities for control and regulation. The researchers suggested that diminishment occurs due to the reduction of chlorine to chloride by H_2O_2, which halts further reaction of chlorine with dissolved organic matter and other DBP precursors. However, further research was needed to quantify the chlorine to chloride ratios, rate constants and kinetics. The reduction in DBPs resulting from the use of primary plus secondary disinfectants was found to occur over a wide range of temperatures, pH, bromide concentrations, and dissolved oxygen content (DOC) levels. Using ozone, formation of THMs and formation of inorganic by-products (e.g., bromate) was also diminished, albeit the latter not as strongly. However, the addition of H_2O_2 appears to cause the formation of low levels of several aldehydes and ketones similar to those formed by the ozonation. A total of 13 aldehydes and six ketones were identified as H_2O_2 DBPs in synthetic water.

Health Risk Estimates and Related Studies: Widespread use of the combined disinfectant, if ultimately deemed practical, might result in potential for uptake of silver ions by exposed fish and humans with corresponding potential health risks. An environmental fate and transport model was developed and used to simulate silver partitioning between water and sediment, uptake by algae, invertebrates and fish (trout and carp), and risks to humans resulting from contaminated fish consumption. Monte-Carlo simulations were used to represent the uncertainty and variability of input parameters. The modeling effort used a variety of scenarios, including "worst case" conditions in which receiving waters provided small amounts of dilution, and subsistence fishers consumed large amounts of high trophic level feeders. The results suggested that public health risks are minimal under all likely scenarios and water treatment with Ag^+ poses no significant health risks through any exposure pathways.

Investigators

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For More Information

NCER Project Abstract and Reports:

http://cfpub2.epa.gov/ncer_abstracts/index.cfm/fuseaction/display.abstractDetail/abstract/198/report/0

Peer Reviewed Publications

Glezer, V., Harris, B., Tal, N., Iosefzon, B., and Lev, O. 1999. Hydrolysis of haloacetonitriles: Linear free energy relationship, kinetics and products. Water Research 33(8):1938-1948.

Armon, R., Laot, N., Lev, O., Shuval, H., and Fattal, B. 2000. Controlling biofilm formation by hydrogen peroxide and silver combined disinfectant. Water Science and Technology 42(1-2):187-192.

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Batterman, S., Zhang, L.Z., and Wang, S.Q. 2000. Quenching of chlorination disinfection by-product formation in drinking water by hydrogen peroxide. Water Research 34(5):1652-1658.

Pedahzur, R., Katzenelson, D., Barnea, N., Lev, O., Shuval, H.I., Fattal, B., and Ulitzur, S. 2000. The efficacy of long-lasting residual drinking water disinfectants based on hydrogen peroxide and silver. Water Science and Technology 42(1-2):293-298.

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Batterman, S., Zhang, L., Wang, S., and Franzblau, A. 2002. Partition coefficients for the trihalomethanes among blood, urine, water, milk and air. Science of the Total Environment 284:237-247.